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SOURCE Zhurnal Fizicheskoy Khimii, Vol XXIII, No 10, 1949.NATURE OF BOND AND DIPOLE MOMENT OF THE LiH MOLECULE

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A description of the character of the bond as a superposition of homopolar and ionic bonding is a very useful approximation in quantum-mechanical research on the properties of molecules. Such a description, for example, has already made it possible to explain the observed values for the dipole moments of molecules with bonds of the intermediate type [1]. Even for such a typically homopolar molecule as the hydrogen molecule, regarding the bond as partially ionic noticeably improved the conformity of theoretical and experimental values for the bond energy and polarizability [2]. In the case of ionic molecules, it is sometimes also expedient to allow for a correction dependent on the homopolar structure.

The coefficients for the terms of the wave function, corresponding to the different structures, should be determined, generally speaking, by the perturbational or variational method of calculating the bond energy. However, for complicated molecules, the variational calculation entails practically insurmountable difficulties. That is why, in the calculation of such molecules, various simplifying assumptions are made which rarely can be rigidly justified. For a roughly approximate estimation of the ionizability of the bonds of complicated molecules, experimental data on the dipole moments or bond energies are used.

Variational calculation of the bond energy of the simplest polar molecule, the lithium hydride molecule, was carried out. The structure of the bond was described by an atomic-ionic wave function, that is, the bond was regarded as partially ionic.

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The comparative simplicity of the function used made computation of the various molecular constants feasible for practical purposes, and made it possible to explain the effect of individual electron cloud structures on the results of the computation. Calculations of the LiH molecule, which have been made up to the present time [3], have not been based on the atomic-ionic wave function, and therefore do not permit predictions concerning the degree to which the bond is ionizable, the role of the individual structures, the dipole moment of LiH, etc.

In the LiH molecule, it may be assumed with sufficient accuracy that the bond is formed by two electrons, since, besides the outer electrons composing the bond, there is only a closed layer of inner electrons in the lithium atom. Assuming that the bond is formed by two electrons, it is only necessary to maintain the orthogonality of the wave function of the inner and outer electrons [4]. The unique electron configuration of the LiH molecule permitted the use of equations corresponding to the method of the incomplete separation of variables [5], in which the wave function is made up of the one-electron function of the inner and the two-electron function of the outer electrons. The LiH molecule is analogous to the beryllium atom in the distribution of electrons. There is a very accurate calculation of this atom, according to the method of incomplete separation of variables, which includes the distance between the electrons  $r_{1,2}$  in to the wave function of the outer electrons [6]. The atomic-ionic function, used in this article and composed of one-electron functions, does not include the obvious dependence on  $r_{1,2}$  and, for that reason is not a single two-electron function in the usual sense. The only significance of the method of incomplete separation of variables lies in the fact that it permitted the use of several known equations.

The wave function used here to describe the state of the outer electrons of the LiH molecule, in the variational calculation of the bond energy before orthogonalization, had the form:

$$\Phi(1,2) = \psi_0(1)\psi_2(2) + \psi_0(2)\psi_2(1) + a\psi_0(1)\psi_0(2) + b\psi_2(1)\psi_2(2), \quad (1)$$

where  $a$  and  $b$  are the variable coefficients characterizing the weight of the structure. The following analytical expressions were used as one-electron functions:

$$\begin{aligned} \psi_0 &= \sqrt{\frac{\gamma^3}{\pi}} e^{-\gamma r_a}, \\ \psi_1 &= \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha r_b}, \\ \psi_2 &= \sqrt{\frac{3\beta^5}{\pi(\alpha^2 - \alpha\beta + \beta^2)}} e^{-\beta r_b} \left(1 - \frac{\alpha + \beta}{3} r_b\right), \end{aligned} \quad (2)$$

where  $\alpha$ ,  $\beta$ , and  $\gamma$  are the parameters of the atomic functions, and where  $r_a$  and  $r_b$  are the distances of the electron from the hydrogen and lithium nuclei, respectively.

The functions  $\psi_1$  and  $\psi_2$  were suggested by Fok and Petrashen' [7] for calculation of the lithium atom. The function  $\Phi(1,2)$  takes into account the ionic structures  $\text{Li}^+\text{H}^-$  and  $\text{Li}^-\text{H}^+$  along with the homopolar structure. For orthogonalization, according to the equations corresponding to the method of incomplete separation of variables, comparatively small terms containing factors of the integral of superposition  $S_{0,1} = \int \psi_0 \psi_1 d\tau$  were added to the function  $\Phi(1,2)$ . The orthogonalized function has the following form:

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$$\psi(1,2) = \psi_0(1)\psi_0(2) + \psi_0(2)\psi_0(1) + a\psi_0(1)\psi_0(2) + b\psi_0(1)\psi_0(2) - S_{0,1}[\psi_0(1)\psi_0(2) + \psi_0(2)\psi_0(1)] + aS_{0,1}[\psi_0(1)\psi_0(1)\psi_0(2) - \psi_0(1)\psi_0(2)\psi_0(1)] \quad (3)$$

The coefficients a and b will be called the weight factors as previously, although in actuality the function (3) is somewhat different from the usual atomic-ionic function.

To explain the relative role of the individual structures calculations were conducted also with the wave function, taking only one (the  $\text{Li}^+\text{H}^-$ ) ionic structure into consideration (that is, b equals 0), and with a homopolar wave function (a equals b equals 0). The coefficients for the ionic terms or, more accurately, their relation to the coefficient in the homopolar portion of the wave function were calculated analytically according to the Ritz principle.

For convenience in calculation, the values for the parameters were rounded off to  $\alpha=2.7$ ,  $\beta=0.8$ , and  $\gamma=1$  (for the lithium atom, variational calculation gives  $\alpha=2.694$  and  $\beta=0.7667$ ). Calculations were performed also for the purpose of explaining the effect of small variations in these parameters. Such variation was shown to be of little influence. The internuclear distance was assumed to equal three atomic units (R equals 1.587 Å), which practically conforms to the experimental value R equals 1.6 Å. A simplified calculation was also performed, as a result of which, as distinguished from previous calculations using an exact operator for the molecular energy, the effect of the inner electrons was regarded as being only a potential field of a cloud of negative charges screening the lithium nucleus. The energy of interaction with this field was included in the operator for the energy of the outer electrons. This modification in calculation disregards exchange with inner electrons. The state of the outer electrons was described by functions (3), orthogonal to the function of the inner electrons. Besides this, simplified calculation with the usual atomic-ionic function  $\Phi(1,2)$  was conducted. This calculation cannot be regarded as correct, because the orthogonality of the wave functions is not maintained. Results of calculations are given in the following table:

Table 1. Basic Structure of LiH Molecule

	Calculation with an Exact Operator for Energy			Simplified Calculation with Orthogonal Functions	Simplified Calculation with Non-Orthogonal Functions	Experiment
Coefficients of ionic structures						
a	0	-0.746	-0.663	-0.689	-0.943	--
b	0	0	0.123	0.139	0.119	--
Bond energy in atomic units	0.0372	0.0553	0.0566	0.0511	0.0877	0.0948

Calculation of the ionic structures gave 34 percent of the computed value for the bond energy which, however, comprised only 60 percent of its experimental value. Calculation of the bond energy and the coefficients at atomic terms showed that it is necessary to consider the ionic structure  $\text{Li}^+\text{H}^-$  along with the homopolar structure. Therefore, the bond in the LiH molecule is considered an intermediate type. That portion corresponding to the structure  $\text{Li}^+\text{H}^+$  is very small.

It should be noted that the character of the ionizability of the bond of isolated molecules is generally found to correspond to the tendency towards

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ionization of these molecules in solutions, since both these properties depend on the great difference in the electronegativity of atoms. It is known that the electronegativity of hydrogen is considerably greater than that of lithium. It is also known that as a result of the electrolysis of solutions of hydrides of alkali metals in liquid ammonia, hydrogen is liberated at the anode. Therefore, in the solution there are  $H^-$  anions. These facts serve as indirect confirmation of the author's conclusion regarding the considerable preponderance of the ionic structure  $Li^+ H^-$ . Simplified calculation using the wave function of the outer electrons orthogonal to the function of the inner electrons gave a very small decrease for the computed bond energy, in comparison with the value obtained in the calculation with an exact operator for the energy. Comparison of the results of these calculations again confirms that, in using orthogonal functions, the role of exchange interaction with inner electrons should be small in the chemical bond [4]; that is, the difference between the results of the simplified calculation and the calculation with an exact operator for energy should be small.

No importance should be attached to the considerably greater conformity with experimental data which is obtained in simplified calculation with non-orthogonal functions.

The essential superposition of the ionic and homopolar linkage type, combined with the comparatively large internuclear distance in the LiH molecule, indicates that this molecule should have a significant dipole moment.

Calculation of the dipole moment of the LiH molecule, using a wave function corresponding to the method of incomplete separation of variables, leads to the general equation:

$$\mu = - \int (x_1 + x_2) \psi^2(1,2) d\tau_1 \cdot d\tau_2, \quad (4)$$

where  $\psi(1,2)$  is a unit-normed function describing the state of the outer electrons of the molecule;  $x_1$  and  $x_2$  are the coordinates of these electrons plotted along the axis of the molecule relative to its center.

Using  $\psi(1,2)$  as an atomic-ionic function, for which previously the coefficients were computed in ionic terms, the dipole moment was calculated. In the basic calculation of the dipole moment, no terms were disregarded; only the approximate character of the employed wave function was maintained. The dipole moment was calculated with consideration of both of the ionic structures,  $Li^+ H^-$  and  $Li^- H^+$ , and without consideration of the structure  $Li^- H^+$  [separately 7]. The moment obtained as a result of calculation with a purely homopolar function is also given for comparison in Table 2.

The basic calculation was performed according to the following equation:

$$\mu = \frac{a^2 \mu_a + b^2 \mu_b + \mu_c + 2a\mu_{ac} + 2b\mu_{bc} + 2ab\mu_{ab}}{N}$$

Here:

$$\begin{aligned} \mu_a &= R(1 - S_{0,1}^2 + 4S_{1,0}(1 - S_{0,1}^2)x_{0,1}, \\ \mu_b &= -R, \\ \mu_c &= (S_{0,1}x_{0,1} - S_{0,2}x_{0,2}), \\ \mu_{ab} &= -2S_{0,2}x_{0,2}, \\ \mu_{ac} &= (1 - S_{0,1}^2)(RS_{0,2} - 2x_{0,2})4S_{0,2}S_{0,1}x_{0,1}, \\ \mu_{bc} &= -(RS_{0,2} + 2x_{0,2}), \\ N &= a^2(1 - S_{0,1}^2)^2 + b^2 + 2(1 + S_{0,2}^2 - S_{0,1}^2) + 2abS_{0,2}^2 + \\ &\quad + 4aS_{0,2}(1 - S_{0,1}^2) + 4bS_{0,2}, \end{aligned}$$

Where:

$$\begin{aligned} S_{0,1} &= \int \psi_0 \psi_1 d\tau, & x_{0,1} &= \int \psi_0 x \psi_1 d\tau, \\ S_{0,2} &= \int \psi_0 \psi_2 d\tau, & x_{0,2} &= \int \psi_0 x \psi_2 d\tau. \end{aligned} \quad (5)$$

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The numerical values of the integrals are:

$$\begin{aligned} S_{0,1} &= 0.095 \\ S_{0,2} &= -0.483 \\ X_{0,1} &= 0.097 \\ X_{0,2} &= 0.416 \end{aligned}$$

Comparison with the basic calculation verified the approximate equation [1,8]:

$$\mu = R \frac{a^2 + 2aS_{0,2}}{a^2 + 2(1 + S_{0,2}^2) + 4aS_{0,2}} \quad (6)$$

This equation can be derived from equation (5) by setting  $b$  equals 0 and disregarding the terms containing the integral of superposition  $S_{0,1}$  and the matrix elements  $X_{0,1}$  and  $X_{0,2}$ . The following table shows the results of the calculations:

Table 2. Calculation of Dipole Moment of the LiH Molecule

	Basic Calculation		Calculation According to Equation (6)	
Coefficients of ionic structures				
a	-0.746	-0.663	0	-0.943
b	0	0.123	0	0
Dipole moments in atomic units (a.u. 2.53D)	1.33	1.34	0.34	1.04

These calculations for the dipole moment of the molecule gave a value of the order of 3.5D. Since there is, at present, no experimental data for the value of the dipole moment of lithium hydride, this result cannot be verified experimentally. Approximately half of the value computed for the dipole moment of the molecule results from the specific characteristics of quantum-mechanical calculation requiring exchange integrals in the computation of the bond energy. In other words, in the dipole moment of the LiH molecule, the role of the so-called transitional structure is large.

Calculation showed that the structure  $Li-H^+$  can be disregarded. The dipole moment, originating from the asymmetry of the electron cloud of the homopolar structure, is not a negligibly small quantity ( $\mu$  of the homopolar structure equals 0.34 atomic units).

The basic calculation gives a value for the dipole moment which exceeds the value obtained according to the approximate equation (6) by approximately  $1\frac{1}{2}$  times. The variance in the results of these two calculations is traceable mainly to rejection of the terms containing the matrix element  $X_{0,2}$  and to the use of nonorthogonal functions in the derivation of equation (5).

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